Non-Oxygen Exchange Reaction of Sulfone Group of Phenyl Benzenesulfonate in Acid Hydrolysis

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The hydrolysis of the esters of carboxylic acids has been shown to proceed through reversible addition intermediates both in acid and in alkaline media[1,2]. The alkaline hydrolysis of phenyl benzenesulfonate has been shown by one of us[3] to proceed through a simple S_{N_2} replacement, without involving prior addition of hydroxide ion on the sulfur atom as shown by (A), which was considered earlier as a posibility[4,5].

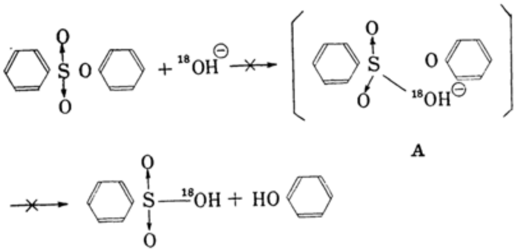

Fig. 1.

Similar studies on the neutral and alkaline hydrolysis of alkyl phosphinic chlorides and phosphorochlorides by Dostrovsky and Halmann[6,7] and of alkyl phosphate by Brutcher and Westheimer[8] have also indicated that these reactions do not proceed via pentacovalent phosphorous intermediates. Recently, however, Haake and Westheimer[9] have shown that the acid hydrolysis of alkyl hydrogen phosphates was accompanied by oxygen exchange similar to that of esters of carboxylic acids. This observation has prompted us to extend our ^{18}O tracer study on the acid hydrolysis of the titled compound. The acid hydrolysis of phenyl benzenesulfonate was very sluggish, more so than that of dimethyl hydrogen phosphate and was found to take place only at above 160°C in a sealed tube using 10 N hydrochloric acid.

An aliquot portion of phenyl benzenesulfonate was added on to 10 N hydrochloric acid diluted with ^{18}O enriched water and the mixture was sealed in a sealed tube. After heating the sealed tube at 180°C for 24 hr., the products, phenol and benzenesulfonic acid were separated by extracting with ether. The ether layer, containig phenol, was treated with bromine to derive 2, 4, 6-tribromophenol, while the aqueous layer was treated with *S*-benzylthiuronium chloride to give the sulfonic acid salt. By these reactions, the hydrolysis was found to give both phenol and benzenesulfonic acid in nearly quantitative yields. In a few separate experiments the reaction was stopped when it was half completed in order to see if the hydrolysis reaction proceeds through a reversible addition intermediate, and unchanged phenyl benzenesulfonate was recovered together with the hydrolysis products.

All these compounds were subjected to ^{18}O analysis by the usual method[10], and the results are shown in Table I.

There was no incorporation of ^{18}O in the recovered ester in this reaction, contrary to the acid hydrolysis of alkyl hydrogen phosphate. This excludes clearly any reversible prior addition of water molecule or hydronium ion in the hydrolysis of this compound and appears to suggest that the reaction is either an S_{N_1} reaction involving a slow cleavage of S–O bond followed by rapid solvolysis to form sulfonic acid or a simple S_{N_2} type synchronous one step process initiated by attack of water oxygen on the sulfur atom similar to the alkaline hydrolysis[3] or on the carbon atom of benzene ring bearing phenolic oxygen.

Since the S_{N_1} type cleavage of sulfur-oxygen linkage will leave additional positive charge on the sulfur atom which bears double formal positive charges, this process would require an enormous enorgy and is quite unlikely to occur. A simple S_{N_2} attack of water or hydronium oxygen on the carbon atom of the benzene

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1) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

2) M. L. Bender, H. Landenhein and M. C. Chen, ibid., **83**, 123 (1961).

3) D. R. Christman and S. Oae, *Chem. & Ind.*, **1959**, 1251.

4) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, **1951**, 1872.

5) C. A. Bunton and V. A. Welth, ibid., **1956**, 3240.

6) I. Dostrovsky and M. M. Halmann, ibid., **1953**, 516, 520.

7) M. M. Halmann, ibid., **1959**, 305.

8) W. W. Brutcher and F. H. Westheimer, *J. Am. Chem. Soc.*, **72**, 2420 (1955).

9) P. C. Haake and F. H. Westheimer, ibid., **83**, 1102 (1961).

10) S. Oae, T. Kitao and Y. Kitaoka, ibid., **84**, 3359 (1962).

Table I. Distribution of thf label in hydrolysis products

Run	Reaction time, hr.	^{18}O atom % of aq. HCl solution	^{18}O atom % of products: Phenol	Benzenesulfonic acid	Recovered ester
1	6	0.42	0.27	0.29 (0.28)*	0.21
2	6	0.80	0.29	0.35 (0.40)	0.21
3	6	1.50	0.78	0.68 (0.64)	0.21
4	24	0.48	0.44	0.35 (0.30)	—
5	24	0.42	0.38	0.29 (0.28)	—
6	24	0.80	0.42	0.41 (0.40)	—

* Numercical values in parrentheses represent theoretical % of ^{18}O atom by the incorporation of one oxygen atom from solvent heavy water.

ring as shown in Fig. 2 also cannot satisfy the results of ^{18}O analysis, because this process will require the phenolic oxygen to be incorporated with the equal amount of ^{18}O to that of the ^{18}O enriched water used, however, this was not the case.

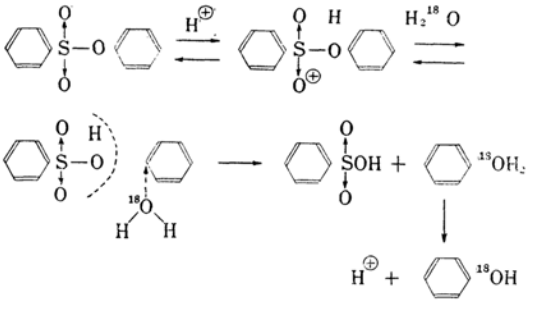


Fig. 2.

Then another, possibly the only, remaining possibility is the S_{N_2} attack of water or hydronium oxygen on the sulfur atom as shown in Fig. 3.

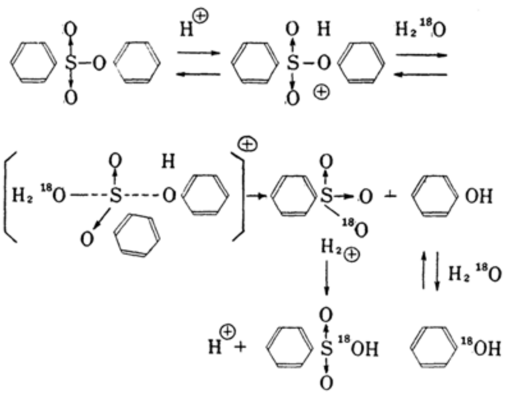


Fig. 3.

If the reaction proceeds through this process, the sulfonic acid will be incorporated with one equivalent amount of ^{18}O and the phenol will remain to be natural just as in the alkaline hydrolysis[3,4,5]. While the sulfonic acid, formed by the hydrolysis, was incorporated with ^{18}O just as much as what is required from this process, phenol was always incorporated with an excess of ^{18}O above the natural concentration and the amount of ^{18}O incorporation appeared to increase with a prolonged heating as shown by Table I.

Table II. Oxygen exchange reaction of phenol and benzenesulfonic acid in the acidic solution

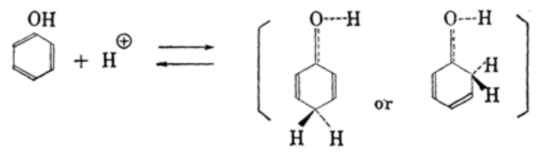
	Reaction time hr.	^{18}O atom % of aq. HCl solution	^{18}O atom % of products
Phenol	5	0.8	0.37
	24	0.77	0.73
Benzene-sulfonic acid	5	0.8	0.23
	24	0.8	0.24

In separate experiments we carried out oxygen exchange reactions of phenol and also benzenesulfonic acid in the same acidic solution. The results are shown in Table II. There was no apparent oxygen exchange in benzenesulfonic acid, even under a prolonged heating, however, all the phenols examined did show rather remarkable oxygen exchange under the condition cited and the amount of ^{18}O incorporation increased with a prolonged heating.

This observation indicates that the phenol formed during the acid hydrolysis of phenyl benzenesulfonate slowly exchange its oxygen with solvent medium.

The overall reaction scheme of this acid-catalyzed hydrolysis of phenyl benzenesulfonate would be the S_{N_2} process in which water molecule attack the sulfur atom, shown by Fig. 3, giving benzene sulfonic acid and phenol that undergoes further slow oxygen exchange with solvent water.

As to the question how phenol exchange its oxygen in acidic medium, we believe that in such a strong acidic medium phenol readily accept a proton at either para or ortho position



B

Fig. 4.

to form a quasi-stable incipient intermediate, B, in which the original hydroxy function aquires more of carbonyl character and hence facilitates the oxygen exchange with heavy water. Incidentally carbonyl group is known to exchange very readily its oxygen in both acidic and alkaline media[11,12].

The carbonyl character of phenolic compounds has been demonstrated only in the case of β-naphthol[13], where β-naphthyl thioglycollic acid was shown to replace hydroxyl group to form. We have also found that other phenols exchange its oxygen in strong acid media.

More detailed investigations on these oxygen exchange reaction of phenols in both acid and alkaline solutions are in progress in our laboratories and will be reported in future.

Experimental

Analysis for Oxygen-18.—Experimental procedure and calculation were similar to those in the previous paper[10].

Phenyl Benzenesulfonate.—This material was prepared by the Schotten-Baumann method[14], and was purified by repeated distillations. The fraction b. p. 152°C/1 mmHg, m. p. 35°C was used.

Hydrolysis of Phenyl Benzenesulfonate in Hydrochloric Acid.—Phenyl benzenesulfonate 1 g. was mixed with 5 ml. of 10 N hydrochloric acid containing water-^{18}O. The mixture was kept for 24 hr. at 180°C in a sealed tube. Then the sealed tube was broken and the whole content was extracted with ether. The ether extract was treated directly with bromine by the usual method, and 1.4 g. of 2, 4, 6,-tribromophenol (m. p. 96°C) was obtained (97 %). In a few experiments, phenol formed by the hydrolysis was repeatedly purified by fractional distillation and subjected directly to ^{18}O analysis.

The aqueous layer was evaporated down to 2 ml.. To this solution was added a few drops of hydrochloric acid and *S*-benzylthiuronium chloride, 0.7 g. and *S*-benzylthiuronium salt of benzenesulfonic acid, 1.2 g. white plate, (m. p. 148.5°C) was obtained. This corresponds to 0.5 g. of benzenesulfonic acid (98% yield).

Partial Hydrolysis of Phenyl Benzenesulfonate in Hydrochloric Acid.—This ester 1 g. was mixed with 5 ml. of 10 N hydrochloric acid containing water-^{18}O. The mixture was heated in a sealed tube for 6 hr. at 180°C. The products were treated as described above. The ether extract was distilled and 0.2 g. of phenol and 0.5 g. of phenyl benzenesulfonate (b. p. 152°C/1 mmHg) were collected.

Isotopic Oxygen Exchange Reaction.—Phenol, 1 g. was mixed with 5 ml. of 10 N hydrochloric acid containing water-^{18}O. An aliquot of the mixture was heated in a sealed tube at 180°C for 5 hr. and the other for 24 hr. Benzenesulfonic acid was also treated in the same way as in the case of phenol.

The exchange products, phenol and benzenesulfonic acid, were derived to 2, 4, 6-tribromophenol and *S*-benzylthiuronium salt, respectively, and these derivatives were subjected to ^{18}O analysis.

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